

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 9/00, 33/08, 33/10, 33/12, 101/02, 57/10, C09D 5/02	A1	(11) International Publication Number: WO 99/18157 (43) International Publication Date: 15 April 1999 (15.04.99)
(21) International Application Number: PCT/US98/21089 (22) International Filing Date: 1 October 1998 (01.10.98) (30) Priority Data: 60/061,049 3 October 1997 (03.10.97) US (71) Applicant (for all designated States except US): UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): VANDEZANDE, Gerald, Anthony [US/US]; 1221 Shincliffe Court, Cary, NC 27511 (US). KAMINSKI, Victor, Vincent [US/US]; 227 Montibello Drive, Cary, NC 27513 (US). DEFUSCO, Andrew, Joseph [US/US]; 218 Solway Road, Lutherville, MD 21093 (US). (74) Agent: WIGGINS, Karen, Johnson; Union Carbide Chemicals & Plastics Technology Corporation, 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US).		(81) Designated States: AU, BR, CA, CN, CZ, ID, JP, KP, KR, LK, MX, PL, SG, US, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SCRUB RESISTANT LATEXES		
(57) Abstract Latex compositions are disclosed which are polymerized from monomers having acid or anhydride functionality and wet adhesion properties. The latex compositions of the present invention can be prepared by a two stage polymerization of a first stage polymer and a second stage polymer wherein a monomer effective to enhance the wet adhesion properties of the composition is included in either the first stage polymer, the second stage polymer, or both.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

SCRUB RESISTANT LATEXES

Field of the Invention

The present invention generally relates to latex polymers and more specifically relates to latex polymers having enhanced wet adhesion characteristics.

Background of the Invention

Latex paint coatings are typically applied to substrates and dried to form continuous films for decorative purposes as well as to protect the substrate. Such paint coatings are often applied to architectural interior or exterior surfaces, where the coatings are sufficiently fluid to flow out, form a continuous paint film, and dry at ambient temperatures.

A latex paint ordinarily comprises an organic polymeric binder, i.e., latex polymer, pigments, and various paint additives. In dried paint films, the polymeric binder functions as a binder for the pigments and provides adhesion of the dried paint film to the substrate. The pigments may be organic or inorganic and functionally contribute to opacity and color in addition to durability and hardness, although some paints contain little or no opacifying pigments and are described as clear coatings. The manufacture of paints involves the preparation of a polymeric binder, mixing of component materials, grinding of pigments in a dispersant medium, and thinning to commercial standards.

- 2 -

Latexes produced for architectural interior or exterior surfaces often require the property of wet adhesion. Wet adhesion is typically tested by casting a 7-mil wet film of the latex paint over a gloss alkyd (oil based) paint film that has been allowed to dry for at least 3 weeks but no longer than 6 weeks. The latex paint is allowed to dry for 24 hours, then the film is cross-hatched, placed in water for 30 minutes, then removed from water and placed on a scrub machine. The cross-hatch section is scrubbed for 500 cycles using a 5% lava soap solution and standard scrub brush. Optimum wet adhesion values are obtained when none of the paint film is removed during the test. The percent film remaining is recorded. Essentially this property allows the paint to adhere to surfaces previously painted with alkyd paints.

One latex polymer commonly used in latex paints which require wet adhesion contains acrylic or styrene / acrylic monomers. Many methods exist to produce latexes from these types of monomers. One particular method utilizes a generic reaction scheme which produces two stage latexes. The first stage is comprised of monomers and chain transfer agents, polymerized in the presence of water and optionally surfactants, to produce a latex polymer which is water soluble or slightly water soluble. A second stage is then polymerized in the presence of the first stage to produce a more hydrophobic polymer. The resultant polymer is referred to in the art as a composite latex with a hydrophobic inner second stage and water soluble or slightly water soluble/swellable outer first stage. In a variation of this procedure, the water soluble/swellable polymer is added concurrently

- 3 -

with the second stage. EP 0 587 333 A2 describes water-resistant multi-stage polymers having an alkali-insoluble polymer and an alkali-soluble polymer which are prepared by sequential emulsion polymerization of a monomer mixture having acid functionality in the alkali-soluble stage and an alkali-insoluble polymer having, optionally, an amine functionality to tie or link the first stage polymer to the second stage polymer.

Functionality has also been incorporated into latexes to allow for crosslinking with other resins. U.S. Patent No. 5,326,843 describes a latex in which hydroxyethyl acrylate is added to the set of polymerizable monomers to impart reactive functionality. The hydroxyl functionality can react with aminoplasts and polyisocyanates to form a cured film. Crosslinkable latexes are also disclosed in WO 95/29963 and WO 95/29944.

Latex polymer compositions comprising blends of latex polymers with wet adhesion properties are disclosed in U. S. Pat. No. 5,208,285. However, the patentees disclose relatively small amounts of carboxylic acid-containing monomers which are often desirable in latex compositions. Accordingly, latex polymer compositions polymerized from monomers having acid or anhydride functionality and wet adhesion properties, i.e., scrub resistance, are desired.

Summary of the Invention

By the present invention, latex polymer compositions polymerized from monomers having acid or anhydride functionality and wet adhesion functionality are provided.

The process of the invention allows for the preparation of a first stage polymer which, upon addition of base, swells, partially dissolves or substantially dissolves the polymer thereby providing a medium for a second-stage polymerization of an alkali-insoluble polymer, providing stability for the alkali-insoluble polymer. The polymer latexes of the of the present invention contain acid contents of up to 10% or higher based on the total weight of the polymer containing the acid or anhydride functionality. Surprisingly, when wet adhesion functionality is added it has been discovered that latex polymers of this type provide excellent wet adhesion when employed in coatings formulations despite the presence of the acid or anhydride functionality.

The present invention provides polymers which can be useful in compositions such as architectural coatings, industrial and automotive coatings, sealants, adhesives, paper coating compositions, inks, varnishes and the like.

Detailed Description of the Invention

The latex compositions of the present invention can be prepared by a two stage polymerization of a first stage polymer and a second stage polymer.

The first stage polymer is an emulsion polymerization of a mixture of monomers comprising at least one carboxylic acid or anhydride functional monomer or monomer that imparts alkaline sensitivity to the first stage polymer, reacted with a variety of comonomers, optionally in the presence of a wet adhesion promoter.

Suitable acid or anhydride functional monomers include acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, citraconic acid, mesaconic acid, itaconic acid, maleic acid, fumaric acid, 3-acrylamido-3-methylbutanoic, acrylic anhydride, methacrylic anhydride, ethacrylic anhydride, crotonic anhydride, citraconic anhydride, mesaconic anhydride, itaconic anhydride, maleic anhydride, fumaric anhydride, p-styrene carboxylic acid, p-styrene sulfonic acids, vinyl sulfonic acid, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, 3-sulfopropylacrylate, 2-acrylamido-2-methylpropane sulfonic acid, and the like including mixtures thereof. In one embodiment of the present invention, the preferred acid monomer is selected from the group consisting of acrylic acid and methacrylic acid.

The amount of acid or anhydride functionality present in the first stage emulsion polymerization determines the degree of solubility of the first stage on addition of a base. A minimum amount of acid or anhydride functionality is needed to solubilize the polymer depending on the hydrophobicity of the comonomers, molecular weight of the polymer, chemical nature of the acid or anhydride monomer and sequence distribution of monomers in the polymers. Acid or anhydride modified polymers can improve or degrade adhesion, depending on the paint system and substrate. When used in excess, acid or anhydride groups render the paint film water sensitive, and thereby hurt wet adhesion. Based on the above criteria, the preferred weight of acid or anhydride functional monomers present in the first stage polymerization is at least about 2 weight percent, preferably at least 3 weight percent, more preferably about 5 weight percent to 50 percent; even more preferably from about 8 percent to 30 weight percent, and most preferably from about 10 percent to 20 weight percent, based on the total weight of monomers charged in the first stage reaction.

Illustrative of comonomers useful in the first stage polymerization are monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate,

- 7 -

styrene, substituted styrene such as alpha methyl styrene, acrylonitrile, vinyl acetate, and other C₁-C₁₂ alkyl or hydroxy alkyl acrylates and methacrylates, vinyl 2-ethylhexanoate, vinyl propionate, vinyl neodecanoate, vinyl neononanoate, vinyl versatate, vinyl pivalate and the like, and/or mixtures thereof.

The first-stage polymer may have a variety of molecular weights. The molecular weight is controlled by the addition of a suitable chain transfer agent as is known in the art. Examples of suitable chain transfer agents include, for example, alkyl mercaptans such as octyl mercaptan and decyl mercaptan, esters of mercaptoacetic acid, such as an ethyl ester of mercaptoacetic acid and 2-ethylhexyl ester of mercaptoacetic acid, and esters of mercapto- propionic acid, such as isooctyl ester of mercaptopropionic acid. In a preferred embodiment, the chain transfer agent may be selected from the group consisting of 2-ethylhexyl mercaptopropionate and iso-octyl mercaptopropionate or mixtures thereof. The number average molecular weight M_n obtained typically ranges from 500 to 100,000.

A wet adhesion promoter is optionally incorporated in the first stage alkali-soluble polymerization to provide wet adhesion properties to the first stage polymer and final latex product. Preferably, the wet adhesion promoter comprises a monomer having nitrogen functionality effective to enhance

- 8 -

the wet adhesion properties of the latex composition.

Preferred wet adhesion promoters include compounds having an amino, ureido or N-heterocyclic group, such as, for example, dialkylaminoalkyl esters and dialkylaminoalkyl amides of acrylic or methacrylic acid, and particularly those having from 1 to 5 carbon atoms in the alkyl groups, free radically polymerizable compounds of urea, ethylene urea, or propylene urea, and polymerizable imidazolidinones having a - NC(O)N - group as part of a cyclic five member ring structure.

Examples of wet adhesion promoters that provide the desired wet adhesion properties include dimethylaminoethyl acrylate, diethylamino acrylate, dimethylaminopropyl acrylate, 3-dimethylamino-2,2-dimethylpropyl-1-acrylate, 2-N-morpholinoethyl acrylate, 2-N-piperidinoethyl acrylate, N-(3-dimethylaminopropyl acrylamide (as used herein includes methacrylamide), N-(3-dimethyl-amino-2,2-dimethyl-propyl)acrylamide, N-dimethylaminomethyl acrylamide, N-(4-morpholinomethyl) acrylamide, N-(2-methacryloyloxyethyl) ethylene urea, methacrylamidoethyl ethylene urea, N-(2-methacryloxyacetamidoethyl-N,N,N',N'-ethylene urea, allylalkyl ethylene urea, N-methacrylamido-methyl urea, N-methacryoyl urea, N-[3-(1,3-diazacyclohexan-2-on-propyl)] methacrylamide, 2-(1-imidazolyl)ethyl methacrylate, 2-(1-imidazolidin-2-on)ethyl methacrylate, vinyl-imidazole, vinylpyrrolidone, and 3-allyl-4,5-methoxy-2-imidazolidinone.

- 9 -

Preferred wet adhesion promoters include N-(2-methacryloyloxyethyl) ethylene urea, and methacrylamidoethyl ethylene urea. In addition, it has been found that propylene imine may be post-reacted with the first-stage alkali-soluble polymer to provide wet adhesion properties and act as a base to neutralize the first-stage alkali-soluble polymer. It can also be reacted to the first stage polymer after the second stage polymer has been formed.

The amount of wet adhesion promoter present in the first stage emulsion polymerization process typically ranges from about 0.1 to 20 weight percent, more preferably from about 1 to 10 weight percent, and most preferably from about 1.9 to 5 weight percent, based on the total weight of the monomer composition of the first stage charge.

In carrying out the emulsion polymerization, at least one initiator or catalyst is used at a concentration sufficient to initiate or catalyze the polymerization reaction. The concentration of initiator and/or catalyst will vary based on the weight of monomers charged. The particular concentration used in any instance will depend upon the specific monomers mixture undergoing reaction and the specific initiator employed; as is well known to those skilled in the art, and is frequently from about 0.01 to 3 weight percent; more preferably from about 0.05 to 2 weight percent and most preferably from about 0.1 to 1 weight percent based on the

weight of monomers charged. It is also known that traces of metal ions can be added as activators to improve the rate of polymerization, if desired. Illustrative of suitable initiators are hydrogen peroxide, peracetic acid, t-butyl hydroperoxide, ammonium persulfate, potassium persulfate, sodium persulfate, as well as any of the other known initiators. Also useful are the redox catalyst systems such as sodium persulfate-sodium formaldehyde sulfoxylate, cumene hydroperoxide-sodium metabisulfite, hydrogen peroxide-ascorbic acid, and the other known redox systems.

The polymerizable feed compositions can also contain any of the other known additives conventionally used in emulsion polymerization processes in the usual known quantities, such as crosslinkers, dispersion aids, emulsifiers, photosensitizers, colorants, bactericides, fungicides, etc.

At the end of the first-stage polymerization, a neutralizing agent or base is added to the first stage alkali-soluble polymer so as to swell, partially dissolve, or substantially dissolve the polymer. Suitable bases include ammonia, triethylamine, monoethanolamine, dimethylaminoethanol, ammonium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide and all other Group I A and II A hydroxides and the like. As discussed above, propylene imine may also be effective for neutralization of the first-stage alkali-soluble polymer, while

- 11 -

at the same time providing wet adhesion properties to the final product.

Based on equivalents of acid in the alkali-soluble polymer, 0.01 to 1.5 equivalents of base are typically added to the alkali-soluble polymer to swell, partially dissolve, or substantially dissolve the alkali-soluble polymer so as to form a stabilized dispersant medium for the second-stage polymerization.

In one aspect of the invention, the first stage latex polymer, as prepared, may be stored for later neutralization. In another aspect of the invention, the first stage polymer can be neutralized and used as a dispersant medium for other latex polymers including the second stage emulsion polymerization process of the present invention.

By using the first-stage polymer as the medium for a second stage emulsion polymerization of alkali-insoluble monomers, the final product has been found to exhibit improved film forming properties, wet adhesion properties and other characteristics.

Monomers useful for polymerization in the second-stage include any alkali-insoluble monomers, i.e., those which are substantially free of carboxylic acid or anhydride functionality, such as, for example, those which have acrylic, styrenic, vinyl or versatic functionality. As used herein, the term "substantially free" means less than about 10 weight percent,

- 12 -

preferably less than about 5 weight percent and more preferably less than about 2 weight percent, based on the total weight of the polymer. Illustrative of such monomers are acrylate and methacrylate esters, styrene, alkyl styrenes, vinyl toluene, vinyl acetate, vinyl alcohol, acrylonitrile, vinylidene chloride, and vinyl ketones. Other illustrative monomers useful in this invention include, for example, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, n-amyl methacrylate, sec-amyl methacrylate, hexyl methacrylate, lauryl methacrylate, stearyl methacrylate, ethyl hexyl methacrylate, crotyl methacrylate, cinnamyl methacrylate, oleyl methacrylate, ricinoleyl methacrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, vinyl propionate, vinyl butyrate, vinyl tert-butyrate, vinyl caprate, vinyl stearate, vinyl laurate, vinyl oleate, vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl isopropyl ether, vinyl n-butyl ether, vinyl iso-butyl ether, vinyl iso-octyl ether, vinyl phenyl ether, a-chlorovinyl phenyl ether, vinyl naphthyl ether, methacrylonitrile, acrylamide, methacrylamide, N-alkyl acrylamides, N-aryl acrylamides, N-vinyl pyrrolidone, N-vinyl-3-morpholinones, N-vinyl-oxazolidone, N-vinyl-imidazole and the like including mixtures thereof.

Optional ingredients which may be included in the second stage polymerization of the alkali-insoluble polymers

- 13 -

include, for example, other monomers such as vinyl esters, acid and/or anhydride functional monomers, crosslinkers, chain transfer agents, and others as known in the art. The number average molecular weight can range from 500 to 500,000 or greater to infinity if the appropriate chain transfer or crosslinking agents are employed. The wet adhesion promoter is also optionally incorporated in the second stage polymerization to provide wet adhesion properties to the final latex product; provided, however, that it is incorporated into at least one of the first stage polymer or the second stage polymer.

The desired ratio for polymerization of the second-stage monomer feed into the first stage polymer medium covers a wide range depending on the desired properties of the final latex composition, and the acid level in each stage. For example, the amount of first stage polymer incorporated into the second stage polymerization may be small when using a more highly carboxylated material [e.g., 10 parts per hundred resin, i.e., first stage plus second stage ("p.h.r.") of the first stage resin which contains 20% methacrylic acid] or larger amount when using a less carboxylated material [e.g., 20 p.h.r. of the first stage resin which contains 10% methacrylic acid]. Suitable ranges include from about 1:99 to about 99:1. Preferably the weight ratio of second-stage monomer feed is

- 14 -

from about 5:95 to 95:5, and most preferably from about 10:80 to 80:10.

The resulting final latex compositions may be used, for example, as binders for architectural coatings, industrial and automotive coatings, sealants, adhesives, paper coating compositions, inks, varnishes and the like.

In paint formulations, the alkali-insoluble polymers dispersed in the first-stage neutralized polymer may be used at levels based on the weight of solids, ranging from about 5 percent to about 90 percent of the total weight of the paint formulation. Paint formulations prepared with these unique polymers have been found to exhibit excellent wet adhesion, high gloss and improved block resistance. The paint formulations may, in addition to the polymers of this invention, contain conventional additives such as pigments, fillers, dispersants, wetting agents, coalescents, rheology modifiers, drying retarders, biocides, anti-foaming agents and the like.

The following description is a general description of an emulsion polymerization process for preparing alkali-insoluble polymers dispersed in substantially dissolved alkali-soluble polymer. In a typical reaction, the mixture of acrylic or methacrylic acids, acrylate or methacrylate esters, and/or styrenic monomers, the wet adhesion monomer, and other optional ingredients are fed to a reactor where they are

emulsion polymerized in the presence of a chain transfer agent and initiator. Typically the polymerization is carried out using a surfactant or emulsifying agent and in aqueous medium. The temperature can vary from about 35°C to about 90°C or higher; the preferred temperature is from about 70°C to about 85°C. The pressure is not critical and is dependent on the nature of monomers being employed, normally gaseous monomers requiring superatmospheric pressures. At the conclusion of the first stage monomer feed, the reaction is held at reaction temperature until the residual monomer level is less than about 5000 ppm, followed by addition of the desired neutralizing agent until the first-stage polymer is swollen, partially dissolved, or substantially dissolved. The second-stage monomers, including optional ingredients such as wet adhesion monomers, are then fed into the first-stage polymer medium at the temperatures described above. At the end of the second-stage monomer feed, the reactor is held at temperature for about one (1) hour, cooled and the latex product collected. Optionally the latex may be further neutralized at this time.

Examples

The examples which follow are intended to further illustrate the invention and should not be interpreted in any manner as limiting the scope of the present invention.

Example A: Synthesis Of Styrene Acrylic Polymer

A monomer mixture was prepared by charging 100 grams of styrene, 70 grams of methyl methacrylate (Aldrich), 30 grams of methacrylic acid (Aldrich), and 7 grams of 2 - ethylhexyl mercapto propionate (Hampshire Chemicals) to a one 1-liter monomer feed cylinder. A second monomer mixture was prepared by charging 210 grams of styrene, 250 grams of methyl methacrylate (Aldrich), 330 grams of butyl acrylate (Union Carbide), and 50 grams of a 25 weight percent of N-(2-Methylacryloyloxyethyl) in methyl methacrylate (ROHAMERE 6844-0) (Rohm Tech) into a second one-liter monomer feed cylinder. A two liter jacketed resin flask equipped with a four - bladed stainless steel mechanical stirrer, Claisen connecting tube, Friedrichs water condenser, nitrogen sparge and bubble trap, thermometer, and monomer addition inlets was used to charge 925 grams of water, 2.5 grams of GR-9M (Union Carbide).

An initial oxidizer solution, prepared by dissolving 2.5 grams of ammonium persulfate in 20 grams of water, was prepared in a separate container. A delayed oxidizer solution,

- 17 -

prepared by dissolving 5 grams of ammonium persulfate in 100 grams of water, was also prepared in a separate container. Under nitrogen purge, the reactor was heated to 80°C by circulating temperature controlled water through the reactor jacket.

After the temperature of the reactor charge had reached 80°C, the initial oxidizer solution was added to the reactor. Two minutes later, the monomer feed was conveyed to the reaction vessel over a 40 minute period by FMI pumps using 1/8" Teflon tubing with continuous stirring while the reaction temperature was held between 79 - 81°C. The reaction was allowed to proceed at 80°C for an additional fifteen minutes after completion of the monomer feed. To the product was added 20 grams of a 15 weight percent ammonium hydroxide solution. After a further 15 minutes the second monomer mix was fed to the reactor concurrently with the delayed oxidizer solution over 2 hours. The product is held at 80 for 1 hour. To the resulting product was added a further 20 grams of 15 weight percent ammonium hydroxide solution. The product was then cooled to room temperature. The resulting 48% solids content latex has a pH of 8, and a volume average particle diameter of 252 nanometers("nm") as measured with an Microtrac particle size analyzer (Leeds-Northrop).

- 18 -

Three samples were made according to the procedure described above with styrene contents of 30 wt % (A1), 10 wt % (A2) and 20 wt % (A3).

Example B: Paint Production

A pigment grind was prepared by mixing the following ingredients in sequence: 30 grams of water, 40 grams of propylene glycol, 9.0 grams of Tamol 165 dispersant (Rohm and Haas), 2.5 grams of Triton® CF-10 surfactant (Union Carbide Corp.), 1.5 grams of Strodex PK-90, (Dexter), 1.0 grams of AMP-95 (Angus), 2.0 grams Nuosept 145 preservative (Huls), 2.0 grams of Foamaster AP defoamer (Henkel), and 225 grams of TiONA RCL-535 titanium dioxide (SCM). The mixture was ground on a high speed disperser for 20 minutes to provide a fineness of grind of 6+ Hegman Scale.

A paint was prepared by mixing, under moderate agitation the following ingredients in order: 550 grams of latex from Example A, 313 grams of the pigment grind made above, 26 grams Texanol coalescing solvent (Eastman), 10.5 grams Polyphase P-20-T mildewcide (Troy), 13.0 grams Acrysol RM-2020 (Rohm & Haas), 10 grams Butyl Carbitol solvent (Union Carbide Corp.), and 134 grams water.

Example C: Wet Adhesion Testing

Wet adhesion was tested by casting a 7-mil wet film of the latex paint over a gloss alkyd (oil based) paint film that had been allowed to dry for at least 3 weeks but no longer than 6 weeks. The latex paint was allowed to dry for 24 hours, then the film was cross-hatched, placed in water for 30 minutes, then removed from water and placed on a scrub machine. The cross-hatch section was scrubbed for 500 cycles using a 5% lava soap solution and standard scrub brush. The results are listed in Table A below.

Table A

Example	Styrene content	24 hour wet adhesion % remaining
A1	30%	100%
A2	10%	100%
A3*	20%	15%

* Wet adhesion monomer was omitted.

Preferably in accordance with the present invention, the 24 hour wet adhesion value is at least 90%, more preferably 95% and most preferably 100%.

Although the invention has been described with respect to specific aspects, those skilled in the art will recognize that the description is not intended to limit the scope of the claims which follow.

What is claimed is:

1. A latex composition comprising:
 - (i) a first polymer polymerized from at least one acid or anhydride functional monomer; and
 - (ii) a second polymer polymerized from monomers which are substantially free of acid or anhydride functionality: characterized in that at least one of said first polymer or said second is polymerized from a monomer having nitrogen functionality effective to enhance the wet adhesion properties of films formed from the latex composition.
2. The latex composition of claim 1 wherein said first polymer comprises at least 2.0 weight percent of the acid or anhydride functional monomer based on the total weight of said first polymer.
3. The latex composition of claim 1 wherein said first polymer comprises at least 5.0 weight percent of the acid or anhydride functional monomer based on the total weight of said first polymer.
4. The latex composition of claim 1 wherein said first polymer comprises at least 10.0 weight percent of the acid or anhydride functional monomer based on the total weight of said first polymer.
5. The latex composition of claim 1 wherein said first polymer is in a solution form.

- 21 -

6. The latex composition of claim 1 wherein said first polymer is in a swollen or partially dissolved form.

7. The latex composition of claim 1 wherein said first polymer is in a particulate form.

8. The latex composition of claim 1 wherein said first polymer and said second polymer are at least partially copolymerized.

9. The latex composition of claim 1 wherein said acid or anhydride functional monomer is selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, citraconic acid, mesaconic acid, itaconic acid, maleic acid, fumaric acid, 3-acrylamido-3-methylbutanoic acid, acrylic anhydride, methacrylic anhydride, ethacrylic anhydride, crotonic anhydride, citraconic anhydride, mesaconic anhydride, itaconic anhydride, maleic anhydride, fumaric anhydride, p-styrene carboxylic acid, p-styrene sulfonic acids, vinyl sulfonic acid, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, 3-sulfo-propylacrylate, 2-acrylamido-2-methylpropane sulfonic acid, and mixtures thereof.

10. The latex composition of claim 1 wherein at least one of said first polymer or said second polymer is polymerized from at least one comonomer selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate, hydroxy propyl methacrylate, styrene,

- 22 -

substituted styrene such as alpha methyl styrene, acrylonitrile, vinyl acetate, C₁-C₁₂ alkyl or hydroxy alkyl acrylates and methacrylates, vinyl 2-ethylhexanoate, vinyl propionate, vinyl neodecanoate, vinyl neononanoate, vinyl versatate, vinyl pivalate and mixtures thereof.

11. The latex composition of claim 1 wherein said monomer having wet adhesion functionality is selected from the group consisting of dimethylaminoethyl acrylate, diethylamino acrylate, dimethylaminopropyl acrylate, 3-dimethyl-amino-2,2-dimethylpropyl-1-acrylate, 2-N-morpholinoethyl acrylate, 2-N-piperidinoethyl acrylate, N-(3-dimethylaminopropyl acrylamide (as used herein includes methacrylamide), N-(3-dimethyl-amino-2,2-dimethylpropyl)acrylamide, N-dimethylaminomethyl acrylamide, N-(4-morpholinomethyl) acrylamide, N-(2-methacryloyloxyethyl) ethylene urea, methacrylamidoethyl ethylene urea, N-(2-methacryloyl-oxyacetamidoethyl-N,N,N',N'-ethylene urea, allylalkyl ethylene urea, N-methacrylamido-methyl urea, N-methacryoyl urea, N-[3-(1,3-diazacyclohexan-2-on-propyl)] methacrylamide, 2-(1-imidazolyl)ethyl methacrylate, 2-(1-imidazolidin-2-on)ethyl methacrylate, vinyl-imidazole, vinylpyrrolidone, and 3-allyl-4,5-methoxy-2-imidazolidinone.

12. The latex composition of claim 11 wherein said monomer having nitrogen functionality is selected from the group consisting of N-(2-methacryloyl-oxyethyl) ethylene urea and methacrylamidoethyl ethylene urea.

- 23 -

13. The latex composition of claim 1 further comprising a neutralizing agent selected from the group consisting of ammonia, triethylamine, monoethanolamine, dimethylaminoethanol, ammonium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide and propylene imine.

14. The latex composition of claim 1 wherein said monomer substantially free of acid or anhydride functionality is selected from the group consisting of propyl methacrylate, isopropyl methacrylate, butyl methacrylate, butyl acrylate, methyl methacrylate, methyl acrylate, ethyl hexyl acrylate, n-amyl methacrylate, sec-amyl methacrylate, hexyl methacrylate, lauryl methacrylate, stearyl methacrylate, ethyl hexyl methacrylate, crotyl methacrylate, cinnamyl methacrylate, oleyl methacrylate, ricinoleyl methacrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, vinyl propionate, vinyl butyrate, vinyl tert-butyrate, styrene, alpha methyl styrene, alkyl styrene, acrylonitrile, vinyl toluene, vinyl acetate, vinyl caprate, vinyl stearate, vinyl laurate, vinyl oleate, vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl isopropyl ether, vinyl n-butyl ether, vinyl iso-butyl ether, vinyl iso-octyl ether, vinyl phenyl ether, a-chlorovinyl phenyl ether, vinyl naphthyl ether, methacrylonitrile, acrylamide, methacrylamide, N-alkyl acrylamides, N-aryl acrylamides, N-vinyl pyrrolidone, N-vinyl-3-morpholinones, N-vinyl-oxazolidone, N-vinyl-imidazole and mixtures thereof.

15. The latex composition of claim 1 wherein said second stage comprises less than about 5 weight percent of acid or anhydride functional monomers based on the total weight of the second polymer.

- 24 -

16. The latex composition of claim 1 wherein the first polymer is polymerized from methacrylic acid, butyl acrylate, and methyl methacrylate and optionally methacrylamidoethyl ethylene urea.

17. The latex composition of claim 1 wherein the second polymer is polymerized from butyl acrylate and methyl methacrylate and optionally methacrylamidoethyl ethylene urea.

18. The latex composition of claim 1 wherein the first polymer is polymerized from methacrylic acid, styrene, and methyl methacrylate, butyl acrylate and optionally methacrylamidoethyl ethylene urea.

19. The latex composition of claim 1 wherein the second polymer is polymerized from butyl acrylate, styrene, and methyl methacrylate and optionally methacrylamidoethyl ethylene urea

20. A paint composition comprising water, pigment and the latex composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/21089

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L9/00 C08L33/08 C08L33/10 C08L33/12 C08L101/02
C08L57/10 C09D5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 587 333 A (ROHM & HAAS) 16 March 1994 see claims 1-10; table 1 ---	1-20
X	US 5 468 800 A (FOELSCH KARL J ET AL) 21 November 1995 see column 6, line 16-39 ---	1
X	US 5 073 591 A (TSAUR SHENG-LIANG) 17 December 1991 see column 5, line 33 - column 6, line 19; claim 1 ---	1-20
A	EP 0 609 756 A (NAT STARCH CHEM INVEST) 10 August 1994 see the whole document -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 February 1999

Date of mailing of the international search report

04/03/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Giesemann, G

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/21089

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0587333 A	16-03-1994	AT 166657 T	15-06-1998
		AU 674326 B	19-12-1996
		AU 4482493 A	10-03-1994
		BR 9303676 A	14-06-1994
		CA 2104893 A	04-03-1994
		CN 1090290 A	03-08-1994
		DE 69318781 D	02-07-1998
		DE 69318781 T	19-11-1998
		FI 933712 A	04-03-1994
		JP 6145262 A	24-05-1994
		MX 9305121 A	31-05-1994
		NO 932988 A	04-03-1994
		ZA 9306348 A	25-03-1994
US 5468800 A	21-11-1995	DE 9301444 U	09-06-1994
		AT 155145 T	15-07-1997
		DE 59403266 D	14-08-1997
		EP 0609793 A	10-08-1994
US 5073591 A	17-12-1991	US 5053448 A	01-10-1991
		AT 113968 T	15-11-1994
		AU 5923790 A	22-02-1991
		CA 2063423 A	22-01-1991
		DE 69014120 D	15-12-1994
		DE 69014120 T	18-05-1995
		DK 482027 T	24-04-1995
		EP 0482027 A	29-04-1992
		ES 2063364 T	01-01-1995
		JP 2790259 B	27-08-1998
		JP 5500376 T	28-01-1993
		MX 171052 B	27-09-1993
		WO 9101336 A	07-02-1991
EP 0609756 A	10-08-1994	CA 2114246 A	29-07-1994
		JP 7034027 A	03-02-1995